

# NOTE ON A FORM OF SILVER OBTAINED IN THE REDUCTION OF THE SULPHIDE BY HYDROGEN.<sup>1</sup>

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IT is a well-known fact that many of the metals are reduced from their oxides, sulphides, and other compounds by hydrogen at high temperatures.

In the majority of such cases the form in which the metal is set free depends upon its fusibility. When both the metal and its compound are fusible only at temperatures far above that at which reduction by hydrogen occurs, the reduced metal usually retains the form originally possessed by its compound, becoming, however, somewhat more porous. Iron reduced by hydrogen from the oxide, sulphide, or chloride, appears as a porous mass or fine powder. The same is true of platinum and of copper.

In the case of other metals, the character of the original compound may exercise a determining influence on the form of the metal after its reduction.

If silver chloride be heated in hydrogen to about 300° C., reduction occurs with formation of hydrogen chloride. The reduced silver appears as a compact, rounded mass, somewhat rough, and having a moderate degree of luster. On heating precipitated silver sulphide in hydrogen, a decomposition occurs with formation of hydrogen sulphide at about the melting-point of silver chloride (450° C.).

The reaction is slow at this temperature, but is more rapid at a somewhat higher heat. The dull, black powder soon begins to assume a slightly lustrous appearance, and at the same time changes gradually into a mass of tangled wires or threads, which lose the black color of the sulphide and exhibit the luster of highly burnished silver. These vary in thickness from that of the finest hairs to that of coarse sewing-thread. They are so linked and knotted together as to be almost inextricable. Under

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a microscope it can be readily seen that some of these wires are made up of many smaller ones, which are often imperfectly twisted together, giving the appearance of a rope whose strands had become partly untwisted. Closely-wound coils are often visible. Many of the wires seem to have the smaller ones of which they are composed welded into a single wire, the sides of which then have a fluted or grooved appearance. Owing to the open spaces left in such a mass, a considerable expansion occurs during the reduction. In several trials it was found that the volume of the mass of reduced silver was about three times that of the original sulphide. Experiments made with argentite, the native silver sulphide, using a piece about three cm. thick, led to similar results. The facets of the crystalline mass did not change their shape, nor was their luster much diminished, but a great number of fine wires of lustrous silver seemed to grow out from the mineral in all directions.

Silver sulphide heated in natural gas gave results like those obtained in hydrogen.

Stephanite,  $\text{Ag}_3\text{SbS}_4$ , although fusible in hydrogen with evolution of a little hydrogen sulphide, yielded no silver at a temperature of dull redness.

Copper sulphide, artificially prepared, was slowly reduced by hydrogen at about the melting-point of barium nitrate ( $600^\circ$ ) with gradual formation of lustrous threads of copper very similar to those obtained in the case of silver.

The observation that silver and copper may be obtained in the form of wires by reduction of the sulphides is not new.

Opificius (*Chemiker Zeitung*, 1888, 649) announced that such a change occurs.

Bischof (*Annalen der Phys. und Chem.*, 1843, 289) describes experiments in which silver sulphide heated in steam to the temperature of boiling sulphur was reduced, yielding wire silver, the sulphur of the sulphide at the same time being oxidized to sulphuric acid. Bischof compares this change of crystalline argentite into wire-like forms of metal on reduction to the alteration of augite into asbestos.

Hampe (*Chemiker Zeitung*, 1893, 1692) has shown that copper in moss-like forms is produced on heating copper sulphide

with filings of the metal to a temperature above the melting-point of copper. The author supposes that copper is dissolved by the fused sulphide and set free again on cooling, being forced out from the fluid interior through the pores of the nearly solid crust in wires or threads. Similar experiments by this author in heating silver with silver sulphide yielded the metal in form of imperfect crystals instead of wires. It is not easy to account for the fact that silver can assume the form of wires or threads so readily on reduction of the sulphide. The fusing-point of silver is  $500^{\circ}$  higher than the temperature of reduction, and it does not seem possible that the peculiar form of the silver can have been caused by fusion of the metal. Nevertheless, its appearance suggests that it has passed through a liquid or plastic condition. It might seem possible that by the heat of reaction between the silver sulphide and hydrogen silver, at the moment of its reduction, the silver had been heated locally to fusion. The heat of formation of silver sulphide (three calories) is, however, nearly as great as that of hydrogen sulphide (7.2 calories). Hence the heat of reaction could not suffice to fuse the silver. Nor does it seem probable that the quality of ductility of solid silver could be here brought into play, for there is apparently no force which could be supposed to cause a drawing out of the metal. Hampe's explanation, that by being forced out through pores in a solidified and contracting crust, covering a fused interior, copper may have been caused to assume the wire form, cannot apply to silver, for the process here is undoubtedly a gradual one, the sulphide passing without fusion, as reduction occurs, into the form of pure silver wires. The results obtained in laboratory experiments suggest an explanation of one mode of occurrence of native metals in veins.

The wire silver found at Zacatecas, in Mexico, may have originated from reactions of such a character.

Hausmann (*Eng. and Min. Jour.*, May 2, 1890) describes the occurrence near Breckinridge, Summit County, Colo., of native gold possessing the remarkable wire-like forms, with fluted or grooved surfaces, so characteristic of silver and copper produced in the laboratory by the reduction of the sulphides by hydrogen.

The change into the fibrous condition at the temperature of

the puddling furnace, as cast-iron becomes converted by oxidation into puddled iron, may, perhaps, be considered similar to that which occurs in the reduction of silver sulphide by hydrogen.

The complete removal of impurities from the iron requires a temperature approaching fusion, and the fibers resulting as the metal becomes nearly pure are united into a mass.

## THE PROTEIDS OF THE KIDNEY BEAN.

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

(Continued from page 643.)

Another portion of the bean-meal was extracted with a considerable quantity of one per cent. sodium chloride solution; the extract was filtered as clear as possible, and dialyzed in a large vessel containing alcohol. The globulin readily separated after a short time, in well-formed tetrahedral crystals mixed with amorphous matter. This precipitate was filtered off, treated for forty-eight hours with one per cent. sodium chloride solution, filtered clear and again precipitated by dialysis in alcohol, at first quite dilute, but afterwards of gradually increased strength. The substance now separated in large well-formed tetrahedral crystals, the edges of which were slightly curved. This precipitate was filtered off, washed with water, alcohol, and ether, dried and analyzed with results as follows:

PHASEOLIN, PREPARATION 18. CRYSTALS.				
	I.	II.	Average.	Ash-free.
Carbon.....	50.98	....	50.98	52.70
Hydrogen.....	6.56	....	6.56	6.78
Nitrogen.....	16.21	16.10	16.16	16.71
Sulphur.....	0.33	0.29	0.31	0.32
Oxygen.....	....	....	....	23.49
Ash.....	3.27	....	3.27	....
				100.00

As dilute acids precipitate proteid substance when added to the sodium chloride extracts of the ground beans, it was thought desirable to make some preparations by this method. Accordingly an extract was prepared by treating the meal with one per cent. sodium chloride solution, and after clearing as completely